



The effect of chloride ion complexation on reversibility and redox potential of the Cu(II)/Cu(I) couple for use in redox flow batteries

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H I G H L I G H T S

- Complexation with chlorides improves the chemical stability of soluble Cu(I) species.
- Reversibility of the Cu(II)/Cu(I) couple is improved in concentrated chloride media.
- The observed potential of Cu(II)/Cu(I) couple allows its use as catholyte for RFB.

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In this work, the Cu(II)/Cu(I) redox couple is studied as an alternative half-cell electrolyte for Redox Flow Battery (RFB) applications. Copper is an abundant and environmentally friendly material that, in combination with appropriate complexing agents, can be solubilized at high concentrations in aqueous media. The effect of adding chlorides as complexing agents in different concentrations, as well as the effects of temperature, have been examined with the objective of increasing the chemical stability of copper chloro-complexes in solution as well as to improve upon the reversibility of these electrochemical reactions. Also, an important shift in potential towards more positive values has been observed when high concentrations of chlorides are used, deviating approximately 0.5 V from the standard redox potential of this couple. This allows for the application of this copper redox couple as a positive electrolyte for RFB technologies.

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1. Introduction

Renewable power sources such as wind and solar systems represent a well-recognized alternative to fossil fuels due to their nearly inexhaustible and environmentally friendly characteristics. However, their significant disadvantage is related to their intermittent and non-predictable nature. One way of ameliorating the intermittent nature of these renewable power sources is to load level these systems by coupling them to an energy storage device that can be tied to the electric grid [1–3]. Nowadays, there is growing interest in developing new batteries with higher capacities of energy storage. For large energy applications, Redox Flow

Batteries (RFB's) seem to be an ideal choice due to their higher capacity in comparison to most electrochemical storage devices.

These flow batteries represent one kind of an advanced rechargeable battery that utilize the oxidation and reduction of two soluble redox couples for charging and discharging the device. These flow batteries differ from conventional batteries in that the energy-bearing chemicals used in RFB's are not stored inside the battery container. Instead, these chemicals are held in two external tanks and pumped into an electrochemical reactor for either charging or discharging.

Many different types of redox flow batteries have been widely explored and include those based on vanadium, polysulfide–bromine, Zn–Br, Fe–Cr, Zn–Ce, lead–acid and others [4–9]. Unfortunately, RFB's are not widely commercialized at this moment due to the high costs of their manufacturing and operation. Thus, there is a need to explore and develop alternative redox couples that are less costly, geochemically abundant and environmentally benign while at the same time providing higher energy densities.

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This would allow these flow batteries to significantly impact the world-wide energy storage scenario.

In order to achieve large energy densities, RFB's utilize high concentrations of chemicals in both anodic as well as cathodic reactions. These concentrations should exceed 1 M to be effective. This presents problems relating to solubility for the particular chemistry of the redox couple employed. The initial concept of the all-vanadium RBF system was first proposed by Skyllas-Kazacos in 1984. This system utilized concentrations of vanadium between 1 and 2 M in sulfuric acid providing energy densities around 25 Wh kg⁻¹ [5,6]. Different supporting electrolytes for vanadium systems have been explored, including those based on halides for aqueous systems [10] and methanesulfonic acid or ionic liquids for non-aqueous media [11,12]. In order to achieve larger values of energy density for automotive applications, Skyllas-Kazacos also proposed a new vanadium chloride/polyhalide system, having V(III)/V(II) ion concentrations as high as 4 M achieved in a hydrochloric acid supporting electrolyte [10]. However, this acid is unsuitable for the positive half-cell in an all-vanadium system due to chlorine evolution during the reduction of V(V) ions. Thus, an alternative redox couple working in chloride media for the positive half-cell would be an ideal choice to take profit of the high specific energy of VCl₂/VCl₃ couple avoiding cross-contamination problems through the membrane.

More recent investigations address the substitution of the positive V(V)/V(IV) redox couple by Fe(III)/Fe(II) using HCl as supporting electrolyte in order to reduce electrolyte and membrane costs [9]. However, a rapid fading in the cell capacity was observed in this system due to the crossover of the Fe/V ions through the membrane, compromising the coulombic efficiency throughout the cycling [13]. To overcome this problem, a hybrid system with mixed Fe/V ions in the positive half-cell using H₂SO₄/HCl supporting electrolytes was proposed [14]. This system allows one to extend the temperature operation range of the VRB from 10–40 °C to 0–50 °C with reasonable values of energy density up to 23 Wh L⁻¹ while avoiding the cross-contamination problems through the membrane. Unfortunately, only a partial substitution of vanadium ions by iron ions in the positive half-cell is possible. In addition, high-cost perfluorinated polymer based membranes are still necessary due to the presence of highly oxidative V(V) ions. Thus, one of the challenges facing the RFB field should be the total substitution of vanadium ions, at least in the positive half-cell electrolyte by an alternative cost-effective redox couple able to function in chloride media over an extended range of temperatures with reasonable energy density and efficiency values.

The Cu(II)/Cu(I) redox couple proposed in this work is a promising alternative for use in RFB's as copper is abundant and less toxic than most materials currently utilized. Unfortunately, it is well known that at room temperature and pressure, the aquated Cu(I) ion is unstable, and disproportionates to Cu(s) and Cu(II) [15]. However, the Cu(I) oxidation state can be stabilized by forming insoluble compounds or by complexation. Previous studies have shown that in dilute acid chloride solutions dominant Cu(I) complexes are CuCl(aq) and/or CuCl₂⁻, and at higher chloride concentrations high-order chloro-complexes such as CuCl₃²⁻ and/or CuCl₄³⁻ become stable [16].

In this work, the effect of adding chloride as a complexing agent has been studied with the objective of increasing the concentration of copper in solution, as well as to improve the chemical stability and reversibility of electrochemical reactions involving the Cu(II)/Cu(I) redox couple. This paper presents work performed with 1 M copper solutions. A more extensive paper is in preparation which addresses systems 2 M in copper where effects of temperature and solubility as well as physical–chemical properties of the electrolyte are examined in more detail.

2. Experimental

2.1. Electrolyte preparation

Copper electrolytes were prepared from Cu(II) chloride dihydrate (>99% purity, Sigma–Aldrich) salt. The concentration of copper was 1 M in all solutions. In order to increase the concentration of chloride, sodium chloride (>99% purity, Sigma–Aldrich) and calcium chloride (>95% purity, Scharlau) were utilized as supporting electrolytes. In some cases hydrochloric acid was added to reach a pH around 0, which is the natural pH of more concentrated copper–chloride solutions, in order to maintain a constant proton concentration in all the solutions and, therefore, to avoid variations in the CV scan performance due to pH differences.

The Cu:Cl ratio was varied from 1:3 to 1:9 following the compositions listed in Table 1. The initial pH of the solutions, before adding the hydrochloric acid, and the final pH are also indicated for each electrolyte. Calcium chloride was used when the solubility limit of NaCl was reached (Cu:Cl ratio of 1:9).

All solutions were deaerated for 30 min by argon bubbling before starting electrochemical experiments.

2.2. Cyclic voltammetry

Cyclic voltammograms were performed using a Bio-Logic VMP3 multipotentiostat. The experiments were run in a three-electrode electrochemical cell containing 100 mL of solution. The working electrode was a graphite rod (99.999% purity, low density, $d = 3$ mm, Sigma–Aldrich) embedded in Teflon, with an effective area of 1.6 cm² and the counter electrode was a platinum mesh. A Ag/AgCl electrode was used as the reference. In order to eliminate copper adsorbed on the surface of graphite, working electrodes were washed repeatedly with hydrochloric acid and rinsed with abundant distilled water before and after the measurements. Temperature was controlled from 30 to 60 °C by immersing the electrochemical cell in a thermostatic water bath.

Preliminary cyclic voltammetry experiments were performed to determine the potential window of operation. Resulting voltammograms have been analyzed to identify copper charge transfer reactions and to estimate the degree of reversibility of these electrochemical processes in a qualitative manner. For the systematic study of reversibility, cyclic voltammetry studies were conducted for a tenfold increase in the scan rate, from 0.01 to 0.1 V s⁻¹. The initial potential and initial scan direction could dramatically affect peak currents while the peak potential is slightly dependent on the switching potential of the direct scan. Thus, the initial potential was 0.5 V vs. Ag/AgCl, where no reduction peak is observed for Cu(II) and the direct scan was towards more negative potentials such that the reduction of Cu(II) to Cu(I) could be observed prior to scan reversal. Considerations concerning reversibility criteria applied in this work are presented in Section 2.3.

2.3. Reversibility criteria

Despite the fact that different criteria have been suggested for estimating the reversibility of redox couples by cyclic voltammetry [17,18], in this work, we mainly focus on those presented in Table 2.

Table 1

Composition of the different copper–chloride electrolytes prepared, the Cu:Cl ratio was varied from 1:3 to 1:9. All the initial (before adding the hydrochloric acid) and final pH's are indicated.

Cu:Cl ratio	Initial pH	Final pH	[CuCl ₂] (M)	[NaCl] (M)	[CaCl ₂] (M)	[HCl](M)
1:3	1	0	1	0.001	0	1
1:5	0.95	0	1	2	0	1
1:7	0.6	0	1	4	0	0.8
1:9	0	0	1	0	3.5	0

Table 2

Trend of the parameters characterizing linear sweep and cyclic voltammetry responses for uncomplicated electrode processes [17].

Parameter	Reversible process
$I_p/\sqrt{\nu}$	Independent of ν ; $I_p/\sqrt{\nu} = 0.4463$ (F^3/RT) ^{1/2} $n^{3/2} \cdot AD_0^{1/2} C_0$
i_{pa}/i_{pc}	Unity and independent of ν
E_{pa}	Independent of ν
$E_{pa} - E_{pc}$	Independent of ν and equal to: $2.218 RT/nF$ mV ($57/n$ mV at 25 °C)
$E_p - E_{p/2}$	Independent of ν and equal to: $-2.199 RT/nF$ mV ($-56.5/n$ mV at 25 °C)

Where ν is the scan rate, i_{pa} and i_{pc} are the anodic and cathodic peak currents respectively, E_{pa} and E_{pc} are the anodic and cathodic peak potentials, $E_{p/2}$ is the half-wave potential of each peak, n is the number of electrons transferred, A is the geometrical area of electrodes, F is the Faraday's constant, R is the ideal gas constant, T is the temperature, D_0 is the diffusion coefficient and C_0 is the bulk concentration of electroactive species.

To clarify their meaning, most of these parameters are represented in Fig. 1A. Peak potentials (E_{pa} , E_{pc}) and half-wave potentials ($E_p - E_{p/2}$) can be directly obtained from cyclic voltammograms. However, the calculation of peak currents is not straightforward. Complications arise when defining baselines in order to determine peak currents or peak heights. To resolve this difficulty, graphical determination of baselines can be performed by extrapolating background currents as shown in Fig. 1B. Also, analytical methods have been developed to correct reverse scans peak currents, such as the equation suggested by Nicholson for peak current ratio correction in CV for uncomplicated electrode processes [18]:

$$i_{pa}/i_{pc} = (i_{pa})_0/i_{pc} + 0.485(i_{sp})_0/i_{pc} + 0.086 \quad (1)$$

Where i_{pc} is the peak height on the direct scan, $(i_{pa})_0$ is the peak height of the reverse scan, $(i_{sp})_0$ is the decaying current of the direct scan at the switching potential.

In our case, both analytical and graphical approaches show a high degree of uncertainty. As a consequence, results should not be taken as quantitative absolute values, but rather as a means of comparing trends when the studied variables are modified.

3. Results and discussion

3.1. Operating potential window

In order to determine the potential region of the $\text{Cu}^{2+} + e^- \leftrightarrow \text{Cu}^+$ redox reaction; preliminary studies under different potential windows were performed varying the scan rate. As shown in Fig. 2, over a 1.5 V potential window two processes are observed.

Peaks 1 and 2 correspond to the oxidation of Cu(I) and the following reduction of Cu(II) respectively, which are the redox processes of interest in this work. Peak number 3 indicates the formation of solid copper on the surface of the working electrode as, in the negative direction, the current decreases sharply showing the typical nucleation loop that corresponds to the electrodeposition of a metal. The last peak, number 4, indicates the dissolution of copper that was electrodeposited, which oxidizes back to Cu(I).

3.2. Effect of temperature

In Fig. 3, one observes that reversibility is improved by increasing the temperature, since peak potential separation is decreased.

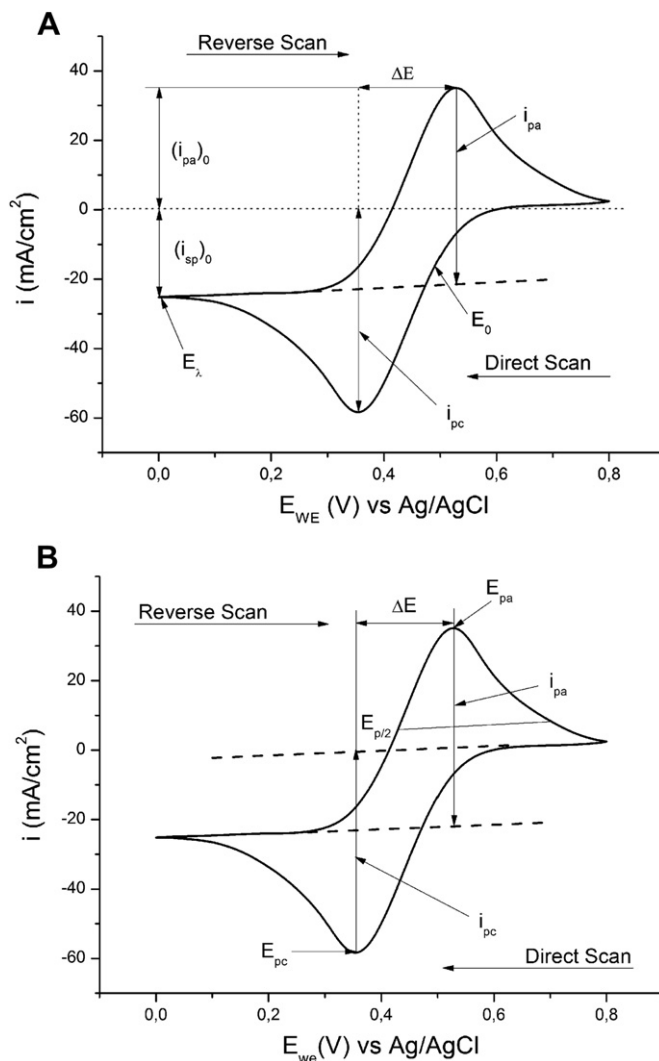


Fig. 1. A) Parameters included in the Nicholson equation; B) Extrapolated background baselines for peak current determination in CV and parameters of interest: Anodic and cathodic peak potentials (E_{pa} , E_{pc}), peak potential separations (ΔE), half peak potentials ($E_p - E_{p/2}$) and peak currents (i_{pa} , i_{pc}).

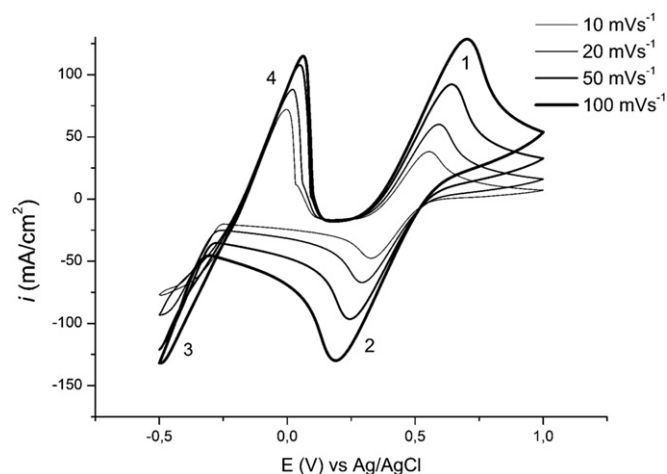


Fig. 2. Cyclic voltammograms of 1 M $\text{CuCl}_2/3.5$ M CaCl_2 electrolyte; the selected Cu:Cl ratio was 1:9; the experiments were performed varying the scan rate, $\nu = 0.01, 0.02, 0.05$ and 0.1 V s^{-1} at 40°C .

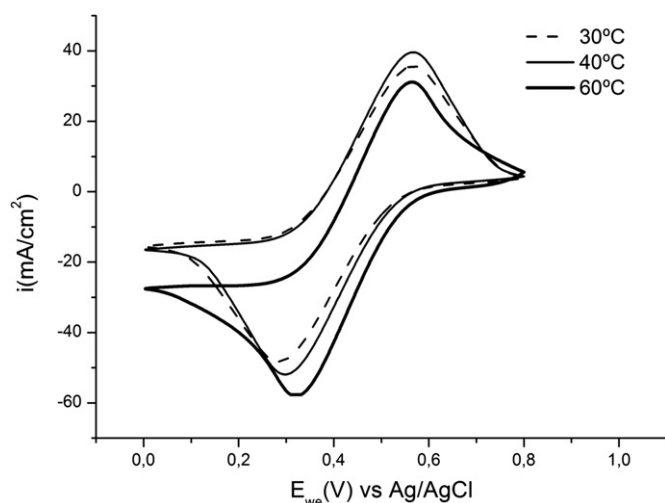


Fig. 3. Cyclic voltammograms of 1 M CuCl_2 /3.5 M CaCl_2 electrolyte; the selected Cu:Cl ratio was 1:9; the experiments were carried out at 0.01 V s^{-1} in a range of temperature of 30–60 °C.

The theoretical peak potential of separation for a reversible CV varies from 58 up to 64 mV over a range of temperatures from 30 °C to 60 °C [17,18]. In the copper–chloride system under study, the experimental separation in peak potentials is 283 mV at 30 °C and 244 mV at 60 °C. Thus, the difference between theoretical and experimental values decreases as the temperature is increased. Provided that the values of peak potential separation are differential, the observed behavior is independent from the changes of the Ag/AgCl reference electrode potential with temperature, that has been assumed to be -0.989 mV K^{-1} [19].

However, absolute peak potentials depend on actual Ag/AgCl reference potential at a given temperature. Once those corrections are made, the position of anodic and cathodic peaks is modified leading to a different interpretation that one can observe in Fig. 3, which is referred to the Ag/AgCl reference electrode without any temperature correction. The differences between cathodic peak potentials and anodic peak potentials over this range of temperatures are 16 mV and 23 mV respectively. Cathodic peak potentials shift towards higher values, while anodic peaks move towards lower values, leading to a lower separation in peak potentials, as mentioned above. Consequently, the degree in reversibility for the overall process is slightly improved at the highest temperature tested.

Literature data indicates that at room temperature, complexation of Cu(II) ions by chlorides is poor and Cu^{2+} , CuCl^+ and CuCl_2 are dominant species, with CuCl_3^- becoming important at high chloride concentrations [20]. With increasing temperature, the dielectric constant of water decreases due to the fast rotations of water molecules. Under these conditions, higher-order chloro-complexes of Cu(II) are formed. Although some discrepancies are found within the literature, there is general agreement that at increasing temperatures, there is a trend towards species of decreased charge and coordination number [21]. The differences in the electrochemical performance at increasing temperatures may be then attributed to the formation of different copper complexes in the solution.

Despite the identification and quantification of these different complexes is beyond the scope of this present work, results presented here illustrate that copper-based electrolytes can be used at temperatures higher than 40 °C, which is the upper temperature limit of the all-vanadium system. Further improvements in

electrochemical performance are found in temperatures up to 60 °C. Additional studies are now in progress over an even wider range of temperature.

A more important issue related to temperature is the solubility of copper species in the electrolyte. All solutions under study were stable from room temperature to 60 °C, hence no solid formation was found in any of the samples over several months. Although not considered in this paper, we note that one should test lower temperatures as well. At 1 M, copper ions have not shown signs of precipitation but further studies, now in progress at increasing concentrations of copper, show that this solid precipitation does take place when the boundaries of solubility are exceeded.

3.3. Effect of the concentration of complexing agent

In this work, increasing quantities of chlorides as complexing agents were added to 1 M Cu(II) solutions in order to observe the effect of chloride concentration on the reversibility of the redox process involved in accordance with the criteria discussed previously.

In Fig. 4, cyclic voltammograms of 1 M CuCl_2 solutions at Cu:Cl ratios of 1:3, 1:5, 1:7 and 1:9 are shown. One observes that, while the anodic peak appears in the same potential region for all chloride concentrations employed, the displacement in the cathodic peak is much more pronounced, diminishing the peak potential separation at higher chloride concentrations and therefore improving reversibility.

When lower chloride concentrations are used, Cu:Cl ratio 1:3, it is not possible to observe a clear peak indicating the reduction from Cu(II) to Cu(I) species. The shape of voltammograms at the lowest chloride concentrations suggests a direct transition from Cu(II) to metallic copper without forming Cu(I), likely because this species is not formed at detectable concentrations. Furthermore, the electrodeposition process is more favorable under these low chloride concentration conditions.

The displacement towards more positive potentials of the anodic peak under increasing concentrations of chloride should be attributed to an increase in the kinetic rate constant of the forward reaction, which is the reduction of Cu(II) species. Since the

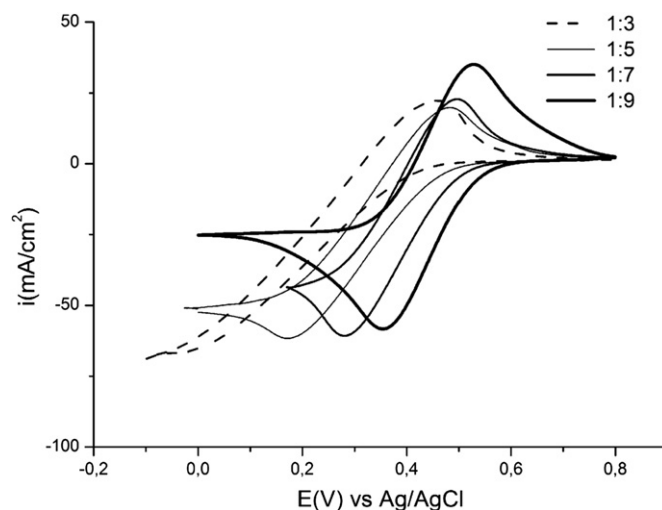


Fig. 4. Cyclic voltammograms of 1 M CuCl_2 electrolytes at increasing concentrations of chlorides; the Cu:Cl ratio was varied from 1:3 to 1:9. The experiments were performed at a scan rate of 0.01 V s^{-1} at 50 °C.

Table 3

Peak potential separations and half-wave potentials for 1 M CuCl₂ at increasing concentrations of chlorides; Cu:Cl ratios from 1:3 to 1:9. The experiments were carried out at 50 °C; Scan rate = 0.02 V s⁻¹.

Cu:Cl ratio	ΔE (V)	$E_p - E_{p/2}$ (V)
1:3	0.57	0.17
1:5	0.31	0.16
1:7	0.31	0.15
1:9	0.31	0.14

coordination number and charge of Cu(II) complexes is decreased at high concentrations of chloride, the mobility of these species might be also modified. For instance, during the reduction process, the working electrode is positively charged. Hypothetically, if the Cu(II) species reach a more negative charge, there is a positive effect on the migration of those species to the electrode surface, improving the mass-transport step. The increase in the rate constant of the half-reaction of reduction may be then enhanced to improve diffusion of Cu(II) species. This effect leads to a higher symmetry in the system, and an improvement in the degree of electrochemical reversibility under these high chloride concentration conditions.

This behavior can be even more clearly observed in Table 3, where the separation in peak potentials, ΔE , decreases as the concentration of chlorides increase. Separations in peak potentials are greater than 59 mV even at very low scan rates, thus indicating the process is quasireversible. Results shown in Table 3, suggest that the degree of reversibility is similar for chloride concentrations above 5 M when the copper concentration is 1 M. In Table 4, we show ΔE values that have been obtained by Skyllas-Kazacos for their vanadium species in chloride media [22]. These values are similar to those related to copper electrolytes shown in the previous table.

Half-wave potential measurements are in agreement with results obtained for separation in peak potentials. For reversible processes, the difference $E_p - E_{p/2}$ should be independent of the scan rate and equal to 61 mV at 50 °C (56.5/n mV at 25 °C) [17]. Taking into account this criteria, as the quantity of chlorides is increased from a Cu:Cl ratio of 1:3 to 1:5, the degree in reversibility is considerably improved. However, for higher concentrations of chloride, the behavior is similar and cannot be further improved in terms of potential.

Peak current ratios (i_{pa}/i_{pc}) are also closer to unity when the chloride concentration is above a Cu:Cl ratio of 1:5 indicating a more reversible behavior. Note that this ratio deviates significantly for lower chloride concentrations as reported in Table 5. It is also noticeable that for a Cu:Cl ratio of 1:3, peak current ratios are higher than unity. Thus, the anodic peak height is larger than that of the cathodic, meaning that some kinetic complications are present in the reduction process at low chloride concentrations.

In general, an ideal reversible behavior can be observed in a process which involves only a charge transfer and a mass-transport step, the former much faster than the latter. Some authors suggest that, for copper systems, deviations from

Table 4

Peak potential separations for 2 M vanadium chloride electrolytes in different concentrations of hydrochloric acid calculated from cyclic voltammograms at 0.02 V s⁻¹.

[HCl] (M)	Electrode	ΔE (V)
5.0	Graphite	0.30
6.7	Graphite	0.40
8.5	Graphite	0.25

Table 5

Peak current ratios (i_{pa}/i_{pc}) for 1 M CuCl₂ electrolytes at increasing concentrations of chlorides; the Cu:Cl ratio was varied from 1:3 to 1:9. The experiments were performed at different temperatures from 30 to 50 °C; scan rate = 0.02 V s⁻¹.

Temperature (°C)	Cu:Cl ratio			
	1:3	1:5	1:7	1:9
30	1.54	0.97	0.93	1.09
40	1.37	0.92	0.88	1.08
50	1.21	0.89	0.88	1.03

reversibility are due to the fact that different adsorption mechanisms of Cu(I) and Cu(II) species are occurring at the electrode surface [23–25]. Those complications on the surface of graphite electrodes could be responsible for deviations in peak current ratios from unity.

Another important diagnostic test utilized in CV is a plot of current function ($i_p/\nu^{1/2}$), where ν is the scan rate. This functional form is related to the fact that, in the absence of kinetic limitations, the rate of charge transfer is diffusion controlled. Fick's second law of diffusion introduces a $\nu^{1/2}$ dependence into the current response. Thus, division of the peak current by $\nu^{1/2}$ removes the diffusional dependence of the current response from the cyclic voltammogram [26]. Results obtained by representing i_p versus the square root of the scan rate show linear behavior regardless of the chloride concentration in the electrolyte. The slopes of these curves can be used to calculate a diffusion coefficient and these coefficients are quite similar for all chloride concentrations explored.

In Fig. 5, the peak current for anodic and cathodic processes of a fixed composition of electrolyte is represented versus the square root of the scan rate.

The slope of the cathodic process is smaller than that of the anodic indicating more mass-transport complications in the former than in the latter reaction, since the diffusion coefficient seems to be lower in this case. This result is in good agreement with the conclusions extracted from Fig. 4, as discussed above. The differences between anodic and cathodic slopes could also be interpreted as differences in the size and charge of the respective copper chloro-complexes reacting at the surface of the electrodes. This may affect the mobility of ions in the diffusion layer when they travel from the bulk solution to the electrode surface and viceversa. In addition, these slope variations between anodic and cathodic

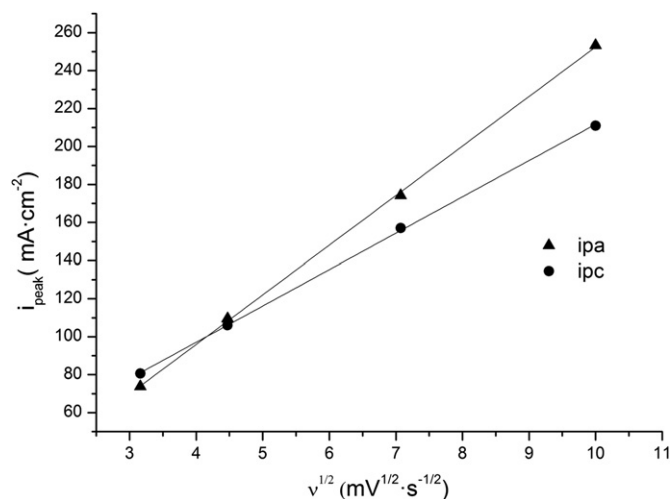


Fig. 5. Anodic and cathodic peak currents of 1 M CuCl₂/3.5 M CaCl₂ electrolyte vs. the square root of the scan rate; the selected Cu:Cl ratio was 1:9; the experiment was performed varying the scan rate from 0.01 to 0.1 V s⁻¹ at 50 °C.

peaks could also reflect kinetic complications resulting from disproportionation of the Cu(I) species, but further investigation should be made to confirm this possibility.

As mentioned previously, the reaction cannot be considered totally reversible in the selected range of scan rates. Consequently, the peak current i_p for an irreversible process is given by [18]:

$$i_p = 0.4958 \left(\frac{\alpha F^3}{RT} \right)^{1/2} n^{3/2} A D_0^{1/2} C_0^* \nu^{1/2} \quad (2)$$

where α is the transfer coefficient, F the Faraday's constant, R the gas constant, T the temperature, n is number of electrons transferred, A the geometric area, D_0 the diffusion coefficient, C_0^* the bulk concentration of electroactive species and ν is the scan rate. A plot of i_p vs. $\nu^{1/2}$ yields a linear relation with a slope proportional to D_0 . Using this relationship, one can estimate the diffusion coefficient. The diffusion coefficient for copper chloro-complexes at a Cu:Cl ratio of 1:9 at 30 °C was found to be $7.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ based on the anodic peak current for the Cu(II)/Cu(I) redox couple. The value of this diffusion coefficient is in accordance to that of free (hydrated)

Cu(II) ions determined at 20 °C which is $7.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [27] and even higher than those reported for V(IV)/V(V) redox couple on graphite electrodes in sulfuric acid [28] and in methanesulfonic acid [11], which are around $2.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature.

Anodic and cathodic peak potential shifts have been analyzed for a tenfold increase in the scan rate, from 0.01 to 0.1 V s⁻¹. In Fig. 6A and B, anodic and cathodic peak potentials are respectively represented and a slight dependence of peak potentials with the scan rate is observed, indicating again a quasireversible behavior. However, the main feature that one gleans from these figures is the noticeable displacement of anodic and cathodic peaks towards much more positive values when the chloride concentration is increased from a Cu:Cl ratio of 1:3 to higher concentrations of complexing agent.

Although the degree in reversibility is neither improved nor damaged by adding increasing concentrations of chloride, a remarkable shift in the formal experimental potential of the Cu(I)/Cu(II) redox couple towards more positive values takes place as this ratio is increased.

As reported in Fig. 7, under the highest concentrations of chloride, the redox process occurs at potential values of approximately 0.5 V more positive than the standard redox potential of Cu(II)/Cu(I) couple, which is $E^0 = 0.153 \text{ V}$ vs. NHE. This is due to the fact that copper ions are not truly free in the electrolyte but are in the form of stable chloride complexes whose redox potential is given by their respective Gibbs free energy of formation. Consequently, the observed redox potential of the system is far away from that of the free Cu(II)/Cu(I) species in absence of chloride ions.

Theoretical values of standard redox potentials of different Cu(II)/Cu(I) chloro-complexes can be obtained from thermodynamical properties found in literature [29–32]. The uncertainties of the available data are large, particularly in the case of Cu(II) chloro-complexes. This makes it difficult to directly compare these data with our actual experiments. None the less, estimations of the theoretical value of the standard potential for the reduction process of cupric species in chloride media have been calculated for different equilibria of stable cupric and cuprous species at

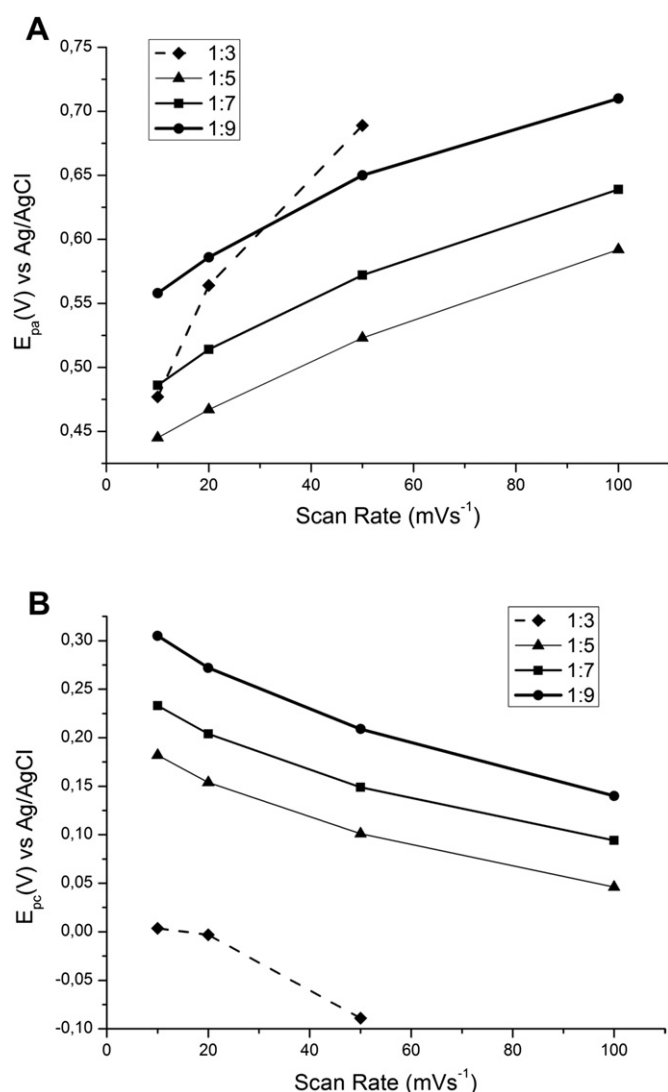


Fig. 6. A) Anodic peak potentials for 1 M CuCl₂ electrolytes at increasing chloride concentrations; the Cu:Cl ratio was varied from 1:3 to 1:9 and the temperature was 50 °C; B) Cathodic peak potentials for 1 M CuCl₂ electrolytes in the same conditions as in 6. A.

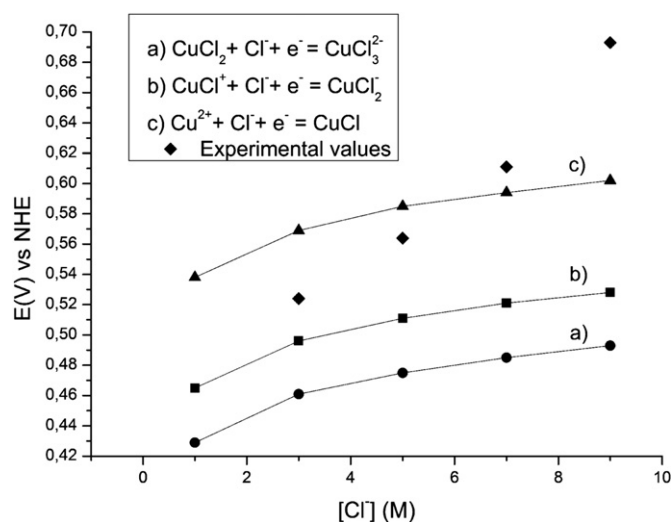


Fig. 7. Experimental formal potential of 1 M solutions of CuCl₂ vs. theoretical redox potentials for different equilibria of stable copper species at increasing concentrations of chlorides. Experimental values were calculated from cyclic voltammograms varying the Cu:Cl ratio from 1:3 to 1:9; $T = 50 \text{ °C}$; a) $\text{CuCl}_2 + \text{Cl}^- + \text{e}^- = \text{CuCl}_3^{2-}$; $\Delta E^0 = 0.429 \text{ V}$ [29], b) $\text{CuCl}^+ + \text{Cl}^- + \text{e}^- = \text{CuCl}_2^-$; $\Delta E^0 = 0.465 \text{ V}$ [29], c) $\text{Cu}^{2+} + \text{Cl}^- + \text{e}^- = \text{CuCl}$; $\Delta E^0 = 0.538 \text{ V}$ [30,32].

increasing chloride concentration conditions [29,32] by applying the Nernst equation. As can be noted in Fig. 7, the observed trend predicts a logarithmic increase of theoretical standard potential towards more positive values under high concentrations of chloride.

However, our experimental values for copper-based electrolytes deviate significantly from those predicted for the different equilibria of Cu(II)–Cu(I) described in literature, especially at the highest concentration of chlorides. This might be due to the presence of multiple copper–chloride redox chemistries concerning copper species that are not considered in the present thermodynamical discussion. For instance, polynuclear complexes involving more than one copper ion could be also present in the mixture, since literature data report the existence of cuprous complexes from CuCl_4^{3-} up to $\text{Cu}_5\text{Cl}_9^{4-}$ [33,34]. At moderate Cu(II) concentrations, 0.5–1 M, polynuclear cupric complexes do not exist in chloride solutions [35–37] but other species of decreased coordination number such as CuCl_3^- or CuCl_4^{2-} could be present if more than one mol of chloride is involved in the equilibria.

Theoretically, the Cu(II)/I–Cl system cannot reach the standard potential of Fe(III)/Fe(II) redox couple, which is 0.77 V. Nevertheless, under actual experimental conditions, the observed potential in the copper–chloride system is close to the formal potential displayed by iron species on a graphite felt electrode in 1.5 M Fe^{2+} /1 M HCl solution, which is approximately 0.5 V vs. Ag/AgCl [13].

4. Conclusions

The degree in reversibility of electrochemical reactions involved in the Cu(I)–Cu(II)–Cl system has been evaluated at increasing chloride concentrations over a temperature range from 30 °C to 60 °C. When the chloride concentration is increased to a Cu:Cl ratio of 1:5 and above, the cathodic peak shifts towards a more positive potential and an appropriate degree in reversibility is achieved in terms of the separation in peak potentials. Those values are comparable and even better than values reported for redox couples widely studied for redox flow batteries, such as V(V)/V(IV).

It was found that an improvement in the degree of reversibility is mainly dependent on the kinetics of the cathodic peak, which is the reduction of Cu(II) to Cu(I). Since lower cathodic peak heights are observed when the concentration of chloride diminishes. This effect is reflected also in the peak current ratios. We suspect that the kinetics and degree in reversibility of this Cu(I)–Cu(II)–Cl system is coupled to some mass-transport complications, particularly during the reduction process. Furthermore, diffusion coefficients of copper species are in good agreement with literature data.

It was also observed that an increase in temperature is favorable for this system since the anodic and cathodic peaks shift towards more reversible potential values, lowering the separation in peak potentials. Although the degree in reversibility is not considerably improved nor decreased with temperature, the thermal stability of the electrolytes allows its use at least up to 60 °C, extending the upper limit of operation of vanadium systems.

Although reversibility is not further improved for Cu:Cl ratios above 1:5, the different species formed at increasing chloride concentrations of copper solutions display an important shift in formal potentials towards more positive values. Due to its standard reduction potential, the redox couple Cu(II)/Cu(I) can be considered

in principle as a negative electrolyte for its application in a redox flow battery. However, in the presence of high concentrations of chloride as a complexing agent, the observed shift in potential of this electrochemical redox reaction to much more positive values opens the possibility of employing copper electrolytes as positive electrolytes that approach the performance of iron electrolytes, that have been widely touted as cheap electrolytes in redox flow batteries.

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